

A New Multiferroic Material: MnWO_4

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Abstract. We report the multiferroic behaviour of MnWO_4 , a magnetic oxide with monoclinic crystal structure and spiral long-range magnetic order. Based upon recent theoretical predictions MnWO_4 should exhibit ferroelectric polarization coexisting with the proper magnetic structure. We have confirmed the multiferroic state below 13 K by observing a finite electrical polarization in the magnetically ordered state via pyroelectric current measurements.

Multiferroic materials which combine magnetism and ferroelectricity currently attract considerable attention [1–4]. There are already several multiferroic materials recently discovered among transition metal oxides: TbMnO_3 [5], TbMn_2O_5 [6], DyMnO_3 [7]. Nevertheless, the search for novel systems with multiferroic properties presents a definite interest. In this letter we report that yet another transition metal oxide, MnWO_4 , belongs to the same class of materials and develops spontaneous electric polarization in a spiral magnetically ordered state [8].

There exist several different microscopic mechanisms which may cause multiferroic behavior [3]. One of the most interesting cases is when a spontaneous polarization exists only in a magnetically ordered phase with a particular type of ordering. This is e.g. the case in TbMnO_3 and TbMn_2O_5 . Microscopic [9] and phenomenological [10] treatments have shown that this happens particularly in spiral magnetic structures with the spin rotation axis \vec{e} not coinciding with the magnetic propagation vector \vec{Q} : theoretical treatment shows that in this case a finite spontaneous polarization perpendicular to the plane spanned by \vec{e} and \vec{Q} may appear

$$\vec{P} \sim \vec{e} \times \vec{Q} . \quad (1)$$

This is not the only source for a magnetically driven ferroelectricity [11, 12], but perhaps the most common one. Accordingly, one strategy to search for new multiferroic materials is to look for magnetic systems with proper magnetic structures. MnWO_4 (also known as the mineral hùbnerite) appears to be just such a system. Detailed studies of the magnetic ordering in this material have shown [13, 14] that below 12.3 K a spiral magnetic ordering develops which seems to satisfy the criterion of Eq. (1). In order to test this we carried out measurements of the dielectric response and of spontaneous polarization of MnWO_4 using single-crystalline samples.

The crystals of MnWO_4 were grown from melt solution. On the basis of earlier work [15] we applied a modified flux technique, using a melt solvent from the system $\text{Na}_2\text{WO}_4 - \text{WO}_3$. The resulting crystals are of dimensions up to $15 \times 5 \times 3 \text{ mm}^3$ and of

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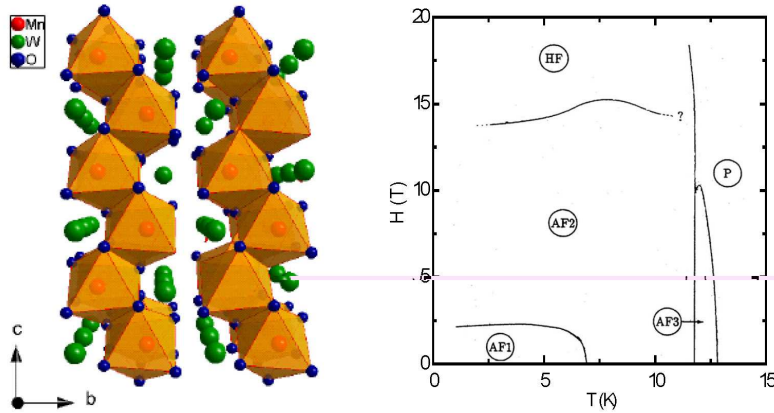


Figure 1. Crystal structure of MnWO₄ and schematic $H - T$ phase diagram for a magnetic field applied along the easy axis according to Refs. [13] and [14], respectively.

dark brown color. The crystal structure of MnWO₄ is monoclinic (space group of the paramagnetic phase P2/c) and consists of edge-sharing [MnO₆] and [WO₆] octahedra that form zig-zag chains along the c -axis, see Fig. 1. Tungsten atoms and manganese atoms are arranged in alternating sheets parallel to (100) [16].

There is apparently also a finite inter-chain coupling causing the observed magnetic ordering below $\simeq 13$ K (see Fig. 1) [13, 14]. According to the previous results there are two separate transitions at 13.5 K and 12.3 K. The upper one is from the paramagnetic state to an incommensurate sinusoidal spin-density wave state, with wave vector $\vec{Q} = (-0.214, 1/2, 0.457)$. The spins are collinear in the ac plane with an angle of about 35° with respect to the a axis. For later use, this direction is termed easy axis. In the so-called AF2 phase below 12.3 K the wave vector hardly changes, but a finite spin component moment along the b axis develops and, as a consequence, an elliptical spiral structure evolves. Finally, a transition to a commensurate magnetic structure with $Q = (\pm 1/4, 1/2, 1/2)$ is found around 8 K, in which the spins are again collinear. Our magnetic measurements, see below, confirm the presence of at least two magnetic transitions, one around 13 K and a second one around 6 K, but we were unable to resolve two separate transitions at 12.3 and 13.5 K. According to Refs. [13, 14] the separate transitions around 13 K can probably be much better resolved by e.g. specific heat measurements than in magnetic data. Moreover, it is reported that the transition to the AF1 phase is of first order and is found between 6.8 and 8 K for different samples and measurement techniques.

With respect to multiferroic behavior, the AF2 phase is the one of interest, because the magnetic structure is a spiral with spin rotation axis \vec{e} different from the wave vector \vec{Q} , which according to Eq. (1) should lead to ferroelectricity. The direction of \vec{e} is given by the cross product of the above-mentioned easy axis and the b axis, and via Eq. (1) we expect a finite polarization in the plane spanned by the easy axis and the b axis with an angle of $\simeq 10^\circ$ with respect to the easy axis.

We used a sample with rectangular (100) surfaces of about 6×4 mm² and a thickness of about 0.7 mm. We have chosen this orientation, since the morphology of our MnWO₄ crystals is dominated by (100). Gold electrodes have been sputtered onto

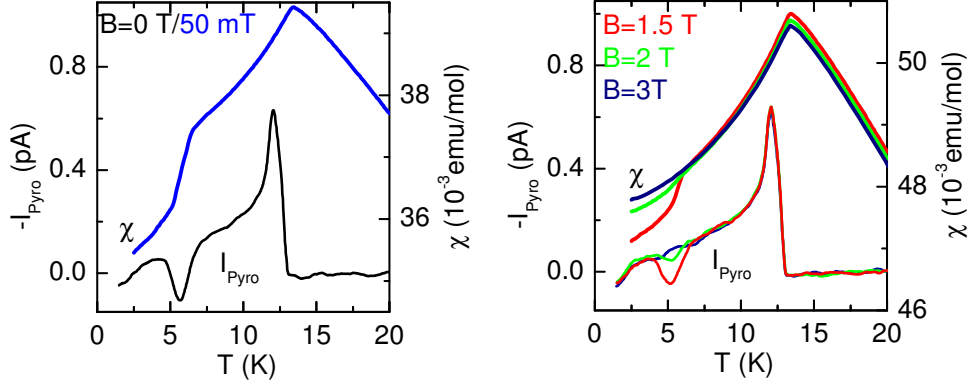


Figure 2. Pyroelectric current I_p (measured along [100], left axis) and magnetic susceptibility χ (right axis) of MnWO_4 measured in zero (or very low) field (left panel) and in higher magnetic fields applied along the c axis.

the opposite faces of the sample, and the dielectric constant ε has been determined by measuring the capacitance of the sample using a precision capacitance bridge (Andeen-Hagerling 2500A). To obtain the polarization \vec{P} , we measured the pyroelectric current I_p using an electrometer (Keithley 6517A), while sweeping the temperature of the sample at a rate of ~ 2 K/min. To avoid domain formation with opposite directions of \vec{P} , we applied an electric field (300 V/mm) while cooling the sample from a temperature well above $T_N \simeq 13$ K. The electric field was removed before the $I_p(T)$ measurements during the heating process. The polarization was determined by integrating the pyroelectric current with respect to the time.

In our measurements of $\varepsilon(T)$ we observed various anomalies in the vicinity of $\simeq 12$ K, i.e. close to the magnetic ordering, but the overall change of $\varepsilon(T)$ remained rather small. The results of the pyroelectric current measurements shown in Fig. 2 reveal that the magnetic transition around 13 K is accompanied by a peak in the pyroelectric current. With further decreasing temperature, this current continuously decreases until another peak of opposite sign occurs around 6 K. The comparison of $I_p(T)$ in zero magnetic field with the magnetic susceptibility $\chi(T)$ measured in a field of 50 mT shows that the anomalies in $I_p(T)$ are clearly related to the magnetic transitions from the PM to the AF3/2 phase and from the AF2 to the AF1 phase, respectively. This correlation is further confirmed by measurements in magnetic fields up to 3 T. As shown in Fig. 2, both $\chi(T, H)$ and $I_p(T, H)$ do hardly change with field in the temperature range above 7 K, while the additional anomalies around 6 K simultaneously decrease with increasing field and vanish for both quantities in a field of about 3 T. In our measurements the magnetic field has been applied along the c axis which means that the contribution of the applied field parallel to the easy axis is $\sim 55\%$. According to Ref. [14] the transition from the AF2 to the AF1 phase is suppressed in fields above about 2 T for this field direction (see Fig. 1). This naturally explains the vanishing of the low-temperature anomalies in both, $\chi(T, H)$ and $I_p(T, H)$ for $H \geq 3$ T.

In Fig. 3 we show the spontaneous polarization calculated via $P(T) = \int I_p(T, t) dt / A$ ($A = 24 \text{ mm}^2$ is the sample surface). Obviously, $P(T)$ continuously

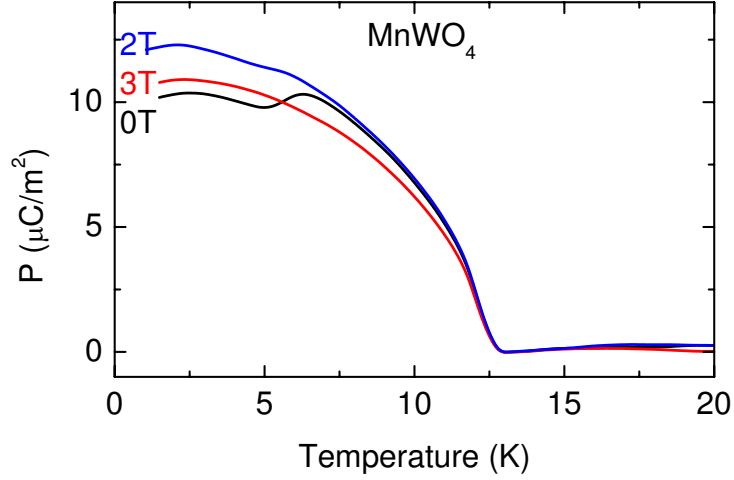


Figure 3. Polarization along the a axis of MnWO_4 for different magnetic fields applied along the c axis.

increases with decreasing $T \lesssim 12.5$ K as it is expected for a standard second-order phase transition. The maximum value of P is of the order of only $10 \mu\text{C}/\text{m}^2$. In our geometry, we measure the projection of \vec{P} onto the a axis. The angle between a and the direction of \vec{P} expected from Eq. (1) is about 36° . Thus, one may expect that the actual value of \vec{P} is about $15 \mu\text{C}/\text{m}^2$, which is more than one order of magnitude smaller than the values observed in other multiferroic materials, as e.g. TbMnO_3 [5], and about 4 orders of magnitude smaller than \vec{P} of typical ferroelectric, e.g. BaTiO_3 [17].

According to Ref. [13], the magnetic structure in the AF1 phase is collinear. From Eq. (1), one should therefore expect a vanishing P in the AF1 phase, while we observe only a partial decrease of P at the AF2-to-AF1 transition in our experiment. One possible explanation for this could be that the finite P arises from one of the other mechanisms, which have been proposed to explain ferroelectricity [11, 12] and may also work within a collinear phase. Alternatively, we cannot exclude that there may be a small content of impurities (e.g. Mn_3O_4) in our sample, which causes only a partial transformation from the spiral and ferroelectric phase AF2 to the collinear phase AF1. Due to the first-order nature of the AF1-AF2 transition, we consider such a phase coexistence as rather plausible, but in order to clarify the real nature of the low-temperature phase further experiments are needed. Moreover, I_P measurements along different axes have to be performed in order to determine experimentally the direction of P .

In summary, we have shown that there appears a spontaneous electric polarization in MnWO_4 below ~ 13 K in the magnetically ordered phase, whose magnetic structure is described by an elliptical spiral. Thus, MnWO_4 is yet another multiferroic transition metal oxide.

Acknowledgments

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References

- [1] Eds.M. Fiebig, V.V. Eremenko, and I.E. Chupis. *Magnetoelectric interaction phenomena in crystals*. Kluwer Acad. Publ. (2004).
- [2] M. Fiebig. Journal of Physics D: Applied Physics **38**, 123 (2005).
- [3] D.I. Khomskii. JMMM **306**, (1.Nov. 2006), cond-mat/0601696 (2006).
- [4] Y. Tokura. Science **312**, 1481 (2006).
- [5] T. Kimura, S. Ishihara, H. Shintani, T. Arima, K.T. Takahashi, K. Ishizaka, and Y. Tokura. Nature **426**, 55–58 (2003).
- [6] N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha, and S-W. Cheong. Nature **429**, 392 (2004).
- [7] T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A.P. Ramirez. Phys. Rev. B **71**, 224425 (2005).
- [8] As we learned recently, the multiferroic nature of MnWO_4 has also been observed independently by T.Kimura *et al.*, and by K.Taniguchi *et al.*, cond-mat/0607481 (2006).
- [9] H. Katsura, N. Nagaosa, and A.V. Balatsky. Phys. Rev. Lett. **95**, 057205 (2005).
- [10] M. Mostovoy. Phys. Rev. Lett. **96**, 067601 (2006).
- [11] N. Aliouane, D.N. Argyriou, J. Stremper, I. Zegkinoglou, S. Landsgesell, and M.v. Zimmermann. Phys. Rev. B **73**, 020102 (2006).
- [12] I.A. Sergienko, C. Sen, and E. Dagotto. cond.-mat/0608025 (2006).
- [13] G. Lautenschlager et al. PRB **48**, 6087 (1993).
- [14] H. Ehrenberg. J. Phys: Cond. Matter **9**, 3189 (1997).
- [15] D. Schultze, K.-Th. Wilke, and Ch. Waligora. Z. anorg. Allg. Chem. **352**, 184–191 (1967).
- [16] H. Weitzel. Z. Kristallogr. **144**, 238–258 (1976).
- [17] F. Jona and G. Shirane. *Ferroelectric Crystals*. Pergamon Press Oxford (1962).